ACCELERATING AND OPTIMIZING PFAS ANALYSIS WITH AN AGILENT eMETHOD

Per- and polyfluoroalkyl substances (PFAS) are a family of over 4,000 synthetic chemicals that have been widely used in food packaging, household products, and various industrial applications in the United States since the 1940s. Due to their carbon-fluorine bonds, PFAS are highly stable and have proved to be resistant to degradation and elevated temperatures. However, their characteristic stability means that PFAS can persist and accumulate in the environment and human body over time, posing serious toxicity concerns.

A common means of exposure to PFAS is through drinking water, typically in close proximity to a facility that makes use of PFAS.

Perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS) are among the most widely studied PFAS, but while their production continues in other parts of the world, their manufacture is no longer permitted in the US, EU and other parts of the world. The import of certain PFAS-containing products into the US is regulated by EPA reviews and the Toxic Substances Control Act (TSCA), but many PFAS products remain unregulated in their use in commercial and domestic products.

Because the full extent of PFAS risks to the environment and human health is still being investigated, it is important that these chemicals can be consistently detected with high accuracy. Reliable, trace-level PFAS data will help inform the regulation of further PFAS compounds used in industry. LC/MS is often used as a means of accurately detecting PFAS at the low levels typically found in the environment. For this purpose, Agilent not only provides solutions featuring ultrahigh performance liquid chromatography (UHPLC) and triple quadrupole mass spectrometry (MS) systems, but also entire turnkey workflows in the form of eMethods, comprising of sample preparation, extraction, quantification, and reporting protocols.

The PFAS eMethod

The PFAS in Drinking and Surface Water by LC/TQ eMethod is verified for the extraction, separation and reliable detection of 100 native and isotopically labeled PFAS in drinking and wastewaters, including 60 PFAS with reported method detection limits. The method includes target compounds that are part of standard methods and regulatory lists such as EPA Method 537.1, EPA Method 533, SW-846 Method 8327, SW-846 Draft Method 8327, ASTM D7979-19, ASTM 7968-17a, ISO 21675:2019, Europe (EU) Water Framework Directive (WfD) & Drinking Water Directive (DWD), Japan Drinking Water Quality Standards, and Germany DIN methods. The Agilent 1290 Infinity II LC and the Agilent 6470 triple quadrupole LC/MS are used in combination to provide high-quality quantitative results. Sample preparation is performed with Agilent SampliQ weak anion exchange (WAX) cartridges, and an Agilent ZORBAX RRHD Eclipse Plus C18 column is used for separation.

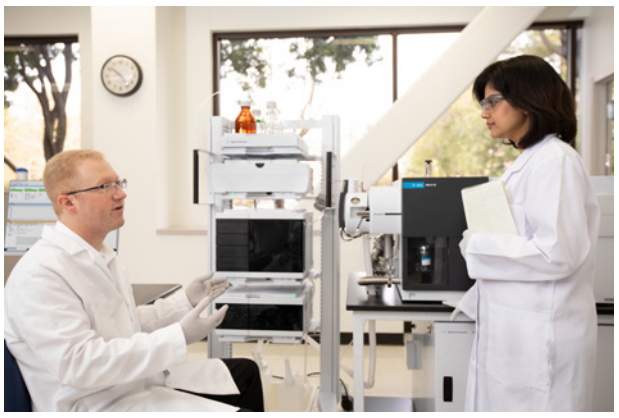
In addition to acquisition and quantitation methods, the PFAS eMethod includes sample preparation protocols, a detailed training video with a step-by-step workflow guide, and references to expertly selected consumables and supplies to minimize cost and effort to design and plan the required analyses.

The eMethod makes use of the Agilent PFAS multiple reaction monitoring (MRM) database for triple quadrupole LC/MS, which features data for over 100 native and isotopically labeled PFAS collected on Agilent Ultivo triple quadrupole LC/MS, Agilent 6470B triple quadrupole LC/MS, and Agilent 6495C triple quadrupole LC/MS systems. The database includes details of the intrinsic properties and identifiers of PFAS such as chemical name, CAS number, and molecular formula. It also features optimized MRM parameters for the analysis of 72 native and 36 isotopically labeled compound from 14 PFAS groups, as well as retention time data from optimized methods.

The eMethod is designed for labs that want a widely applicable testing method and that do not plan to run dedicated regulated methods. For labs running regulated methods, the eMethod in conjunction with the Agilent PFAS MRM database can be a helpful building block to modify existing methods to expand analytical capabilities.

The regulatory landscape

The acceptable limits of PFAS in a variety of matrices—including drinking water, soil, and air—are listed by various regulatory



initiatives worldwide. This regulatory framework is expanding with the increasing numbers of PFAS identified in the environment and differs across regions. Under the EU Drinking Water Directive, 20 PFAS compounds must be monitored in drinking water. The US EPA has also issued advisory limits for PFOS and PFOA in drinking water. In addition, several US states have established their own advisory levels for PFOA, PFOS, and other PFAS.

As a result of continually developing regulations, labs working to develop analytical methods must ensure that they stay up to date with the latest guidance. This proves a considerable challenge, with new PFAS regularly added to regulatory lists and recommended limits in various matrices often lowered.

The current established methods for PFAS quantification vary from each other in terms of the type and number of PFAS analyzed, the matrices studied, the sample preparation technique used, and the detection limits applied. In the US, two EPA methods—EPA 533 and 537/537.1—specifically address quantification of PFAS in drinking water. Both methods make use of solid phase extraction (SPE) followed by analysis using LC/MS/MS, enabling the detection of low concentrations of PFAS. The EPA 8327 and ASTM 7979 methods are specific to PFAS in ground water, surface water, and wastewater; ASTM 7968 is related to analyzing PFAS in soils and solids. Agilent has produced a number of application notes that describe experimental conditions for running each of these methods.

The right analytical techniques

In terms of preferred instrumentation for PFAS analysis, LC/MS/MS using electrospray ionization (ESI) stands as the technique of choice. More specifically, triple quadrupole (TQ) MS instruments generate sensitive, targeted PFAS data, while quadrupole time-of-flight (Q-TOF) MS systems are used to identify novel PFAS. Typically, SPE is applied to extract PFAS from drinking water using an anion exchange resin.

Agilent supplies three triple quadrupole LC/MS systems that can be used to analyze PFAS in environmental matrices: The Agilent

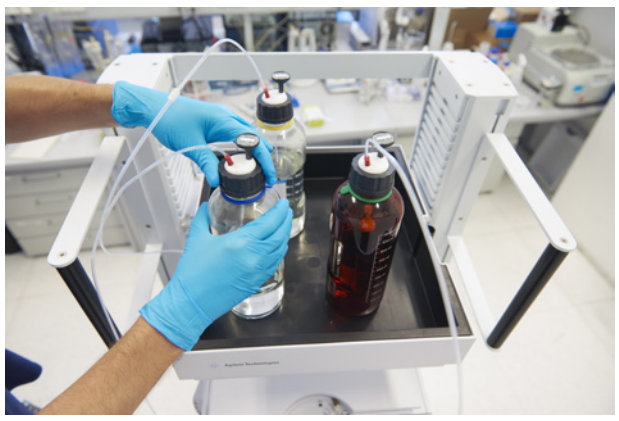
Agilent 6470 triple quadrupole LC/MS

Ultivo triple quadrupole LC/MS is ideally suited to those getting started in LC/MS analysis, providing high accuracy and precision despite its compact size and featuring enhanced maintenance feedback. The Agilent 6470 triple quadrupole LC/MS offers improved sensitivity and facilitates analysis of high matrix samples without requiring substantial cleanup, while reaching exceedingly low levels of detection. In fact, the 6470 LC/TQ was demonstrated to surpass performance requirements for the EPA 8327 and ASTM methods when analyzing PFAS in non-potable water. For even higher performance, the Agilent 6495 triple quadrupole LC/MS enables extremely low limits of quantitation and the simultaneous analysis of several classes of PFAS.

For untargeted PFAS analysis, the Agilent 6546 LC/Q-TOF provides high-resolution measurements with its wide dynamic range and sub-ppm mass accuracy. Complementing the system with Agilent MassHunter and Agilent Mass Profiler Professional software makes it even easier to identify novel PFAS.

The experimental challenges

Analysts are faced with various challenges when attempting to quantify PFAS in the lab. Because of the high numbers of PFAS that have been produced and implemented in applications worldwide, these compounds can be found in a wide variety of matrices. These can include laboratory supplies and instrumentation, which can lead to contamination of PFAS samples and inaccurate results. Certain PFAS are retained on glass, resulting in low recoveries where tools such as glass pipettes are used. Scientists must be aware of how PFAS interact with their instrumentation in order to correctly interpret results, and unwanted PFAS must be consistently removed from labware prior to experimentation. Fluoropolymers used in LC and MS instrumentation must also be accounted for. Agilent supplies a full range of consumables that have been validated as being free of PFAS or having concentrations below typical detection levels for various common PFAS.



Agilent offers a PFC-free HPLC conversion kit for removing PFAS background from LC/MS measurements. The kit includes replacement parts for each section of the LC system that features organic fluorine compounds, as well as an Agilent InfinityLab PFC delay column with Agilent InfinityLab Quick Connect fittings. The solvent lines included in the kit are made of polypropylene and are easy to use due to their flexibility; The Agilent InfinityLab Stay Safe caps are also free of fluorinated materials. The kit is intended for use with an Agilent 1290 Infinity II LC with a high-speed pump and an Agilent 1290 Infinity II Multisampler. The combination of these LC modules provides the best conditions for PFAS analysis, as wash options allow for cleaning of the injection needle, needle seat, and needle seat capillary to minimize carryover from PFAS that may stick to these parts. As a further means of eliminating PFAS background, mobile phase solvents can be filtered using the Agilent InfinityLab Solvent Filtration Assembly prior to analysis.

Further products that help remove unwanted PFAS include Agilent Captiva premium syringe filters, which also limit the sample cleanup necessary before analysis. A weak anion exchange (WAX) resin is also available for drinking water extraction using offline SPE.

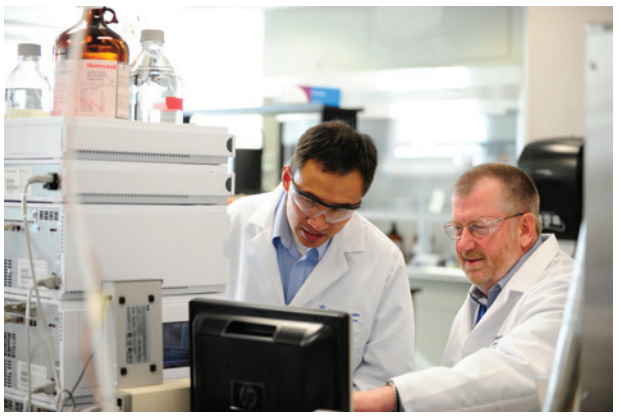
Method development is made challenging by the fact that increasing numbers of PFAS must be quantified at low detection limits and decreasing minimum reporting levels. This requires highly sensitive instrumentation and skilled analysts, who must also often work without validated reference materials, few of which are available for PFAS. To assist in method development, Agilent provides Method & Applications Services to help labs install new instruments, update and optimize existing methods, and train staff appropriately. A PFAS Consumables Ordering Guide is also available, featuring downloadable, customizable lists of the Agilent products required for each regulated method and saving analysts time when ordering supplies.

The future prospects

To keep pace with developing PFAS regulations, it is important for labs to have flexible solutions in place. The 6470 and 6495 triple quadrupole LC/MS and 6546 LC/Q-TOF systems, with their outstanding sensitivity and broad dynamic ranges, provide the flexibility needed to accommodate evolving regulatory requirements. All three instruments have proven reliable through years of service, helping a lab make meaningful long-term plans when investing in these systems.

In time to come, to accelerate sample introduction, there may be more of a shift towards large-volume direct injection or online SPE as a sample preparation method. Agilent LC/Q-TOF systems and the Agilent 1290 Infinity II Online SPE System are well placed to cater to these developments.

The PFAS MRM database can also be used as a means of updating existing methods where necessary, as the number of PFAS it currently list far exceeds those that feature in current regulatory methods. This reduces the time needed to investigate experimental conditions for newly analyzed compounds, enabling analysts to quickly proceed to verification testing and to establish the new method.

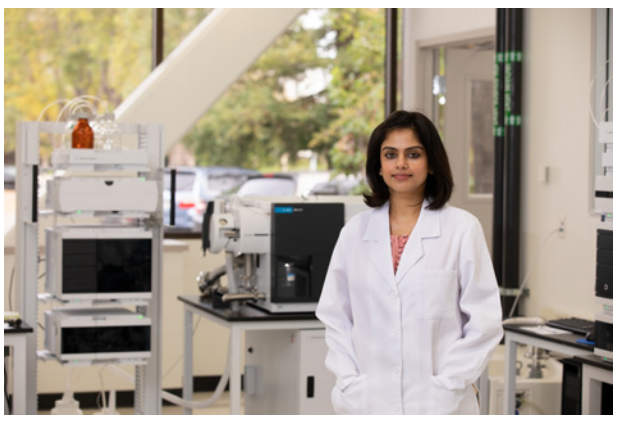


The PFAS in Drinking and Surface Water by LC/TQ eMethod, given the large number of PFAS that it can be used to effectively detect at low levels, also supports labs as they expand their methods with further PFAS target analytes. The eMethod also reduces method development time by providing optimized conditions for the PFAS analysis of interest.

Another potential development may be that isotope dilution for the quantification of PFAS becomes more prevalent. If this is the case, both the PFAS eMethod and Agilent LC/Q-TOF instruments can accommodate isotope dilution well. Due to recent studies demonstrating that PFAS can escape into the air, there is also a need to develop GC/MS methods addressing the air contamination, too. As these methods come into being, the Agilent GC/Q-TOF systems can be applied to effectively analyze PFAS in air at very low detection limits.

The best support in PFAS analysis

Understanding PFAS analytical methods and regulations as well as choosing the right instruments and consumables is key to getting your lab ready for PFAS analysis. The Agilent eMethod makes PFAS analysis using LC/MS accessible to everyone so as to get you up and running in the shortest time possible whilst delivering high quality, accurate and sensitive results.



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